

Influence of pH and irradiation wavelength on the photochemical degradation of sulfonylureas

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Abstract

The photochemical behavior of two sulfonylurea herbicides have been investigated in solution at different irradiation wavelength ranges and pH. Spectrophotometric methods have permitted to determine the pK_a values in the ground state and in the first singlet excited state. Kinetics and quantum efficiency measurements have shown that photodegradation was faster in acidic medium but more efficient in basic medium, when the sulfonylureas were in their ionic form. The identification of the photoproducts and their evolution during irradiations have indicated that three competitive pathways occurred: carbon–sulfur (C–S) cleavage, nitrogen–sulfur (N–S) cleavage, and photohydrolysis of the sulfonylurea bridge. Their preponderance depended on the irradiation wavelengths.

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1. Introduction

Sulfonylureas represent a relatively new and potent herbicide family used by cereals farmers to control broad-leaved weeds and some grasses. Sulfonylureas action consist in inhibiting acetolactate synthase (ALS) which is a key enzyme in the biosynthesis of branched amino-acids (valine, leucine, and isoleucine) in the plant [1]. The most common natural degradation pathways of sulfonylureas include microbial transformation and hydrolysis, but the photodegradation can also play a major role [2–7], particularly at neutral or weakly basic conditions for which these herbicides are less susceptible to chemical hydrolysis.

In recent research [7], we have studied the photodegradation of two sulfonylureas, Cinosulfuron (CiS) and Triasulfuron (Trs), under solar conditions at pH 7. The results have shown that the photodegradation pathway included different cleavages of the bridge, a *O*-demethylation of the triazinic moiety and a *O*-alkylation of the benzenic lateral chain.

In order to better understand the photochemical behavior of sulfonylureas, the present paper reports the influence of pH and irradiation wavelength on the photodegradation of

Cinosulfuron and Triasulfuron. A spectroscopic study of the herbicides and the comparison of the quantum yields, the kinetics and the main degradation pathway under the different experimental conditions are presented.

2. Material and methods

2.1. Reactants

Cinosulfuron [1-(4,6-dimethoxy-1,3,5-triazin-2-yl)-3-[(2-methoxyethoxy)-phenyl]urea] (98% purity) and Triasulfuron [2-(6-methoxy-4-methyl-1,3,5-triazin-2-yl)-1-[2-(2-chloroethoxy)phenylsulfonyl]urea] (99% purity) were purchased from Riedel-de Haën. The 2-amino-4-methoxy-6-methyl-1,3,5-triazine (AMMT) was purchased from Aldrich. All these products were used without further purification.

For fluorescence and photodegradation experiments, pesticides were solubilized in phosphate buffers $5 \times 10^{-3} \text{ mol l}^{-1}$. Exact buffer compositions were: $\text{KH}_2\text{PO}_4 + \text{H}_3\text{PO}_4$ for pH 2–4, $\text{KH}_2\text{PO}_4 + \text{NaOH}$ for pH 5.5, $\text{K}_2\text{HPO}_4 + \text{KH}_2\text{PO}_4$ for pH 7 and $\text{K}_2\text{HPO}_4 + \text{H}_3\text{PO}_4 + \text{NaOH}$ for pH 8–10. As the herbicides were not easy to solubilize in acidic medium, they have been introduced in a small quantity of methanol before adding the phosphate buffers, and this for all pH to ensure the same experimental conditions. In this way, the final solutions contained 4% methanol.

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The water used for buffer preparations was purified with a Millipore water purification system (MILLIQ-50 18 M Ω).

2.2. UV-absorption and fluorescence emission

The UV absorption spectra were recorded with a double beam UVIKON 930 spectrophotometer (Kontron Instruments) and fluorescence spectra on a Kontron SFM 25 fluorometer.

2.3. Irradiation experiments

The irradiation experiments were carried out with two HPK 125 W Philips medium mercury pressure UV lamps, equipped with 50 ml cylindrical reactors, open to air and with an optical window of 11 cm² area. With the first lamp, we used a Pyrex reactor in which the irradiation wavelengths reaching the solution were higher than 290 nm, and with the second lamp, we used a quartz reactor in which the lowest wavelengths reaching the photoreactor were 220 nm. Temperature was maintained at 20 °C with a water circulation system and volumes of 40 ml of herbicides solution were irradiated. For both conditions of irradiation, the photon flux received by the solutions was evaluated with uranyl oxalate actinometry [8]. With the Pyrex reactor, the photon flux was 2.0×10^{17} photon cm⁻² s⁻¹ and it was 1.7×10^{16} photon cm⁻² s⁻¹ with the quartz reactor.

2.4. HPLC analyses

High Pressure Liquid Chromatography. Diode Array Detector (HPLC.DAD) analyses were performed with a Shimadzu VP series HPLC. The column was a Hypersil BDS C₁₈, 5 μ m, (125 \times 4) mm, the flow-rate was 1 ml min⁻¹, the injection volume was 20 μ l, the mobile phase was methanol (A) and water (B) pH of which was set up to 2.80 using H₃PO₄. For herbicide kinetics, isocratic elution conditions were used: 60% (B) for cinosulfuron and 55% (B) for triasulfuron. For photoproducts evolution, the following gradient was used: 95% (B) at $t = 0$ min to 50% (B) at $t = 30$ min, then 50% (B) during 10 min.

3. Results and discussion

The two sulfonylureas used in this work were Cinosulfuron and Triasulfuron. They contain a benzenic derivative, a sulfonylurea link and a s-triazinic system (see Fig. 1).

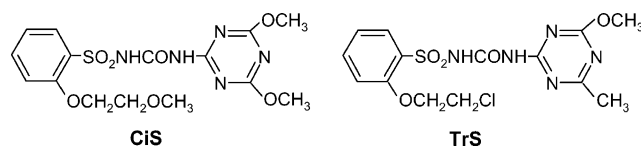


Fig. 1. Absorption spectra of CiS and TrS.

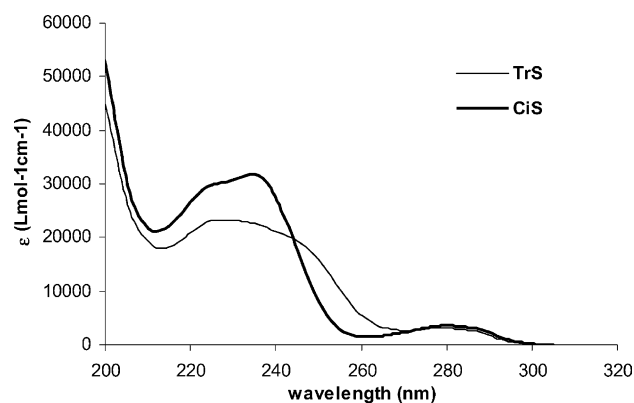


Fig. 2. Molecular structures of CiS and TrS sulfonylureas.

3.1. Absorption spectra of sulfonylureas

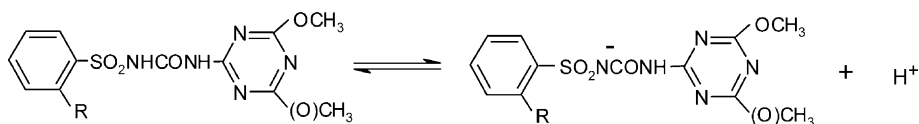
The UV absorption spectra of the two herbicides have been measured at pH 5.5 (Fig. 2). CiS and TrS absorption spectra show two electronic bands: a medium intensity band (I) around 230 nm and a low intensity band (II) centered on 280 nm. As sulfonylureas were insoluble in non-polar solvents such as cyclohexane, the effect of solvent polarity, which could inform on the type of transition, could not be deeply investigated. However, a 7 nm blue shift was observed for the band (I) while passing from water to acetonitrile. Based on this shift, and on the high extinction coefficient (about 30,000 l mol⁻¹ cm⁻¹), the band (I) could be assigned to a $\pi \rightarrow \pi^*$ transition. The absorption range of both CiS and TrS exceed 290 nm, indicating that they were likely to undergo transformations under the two illumination conditions.

3.2. Influence of pH

The influence of the pH on the absorption and on the kinetics of CiS and TrS has been evaluated under the conditions of irradiation in the Pyrex reactor.

3.2.1. Influence of pH on absorption spectra

Sulfonylureas are weak acids with an acid–base equilibrium that can be represented as follows [9,10]:



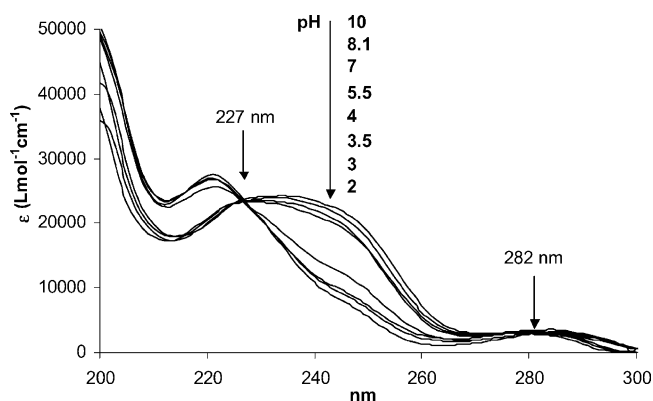


Fig. 3. UV absorption spectra of TrS as a function of pH (initial concentration $3.5 \times 10^{-5} \text{ mol l}^{-1}$). Evidence of two isobestic points.

We have considered CiS and TrS UV absorptions as a function of the pH. The UV absorption spectra present two isobestic points reflecting the presence of two acid–base equilibrium (see the example of TrS in Fig. 3). These isobestic points are located respectively at the wavelengths 223 and 282 nm for CiS and 227 and 282 nm for TrS spectra.

The ground state ionization constant $\text{p}K_a(S_0)$ was calculated using the standard formula [11]:

$$\text{p}K_a(S_0) = \text{pH} - \log \frac{A_{\text{SuH}} - A}{A - A_{\text{Su}^-}} \quad (1)$$

where A represents the absorbance of a solution containing both the acid and the basic forms of the sulfonylurea (noted SuH and Su^-), A_{SuH} the absorbance of a solution of pure SuH and A_{Su^-} the absorbance of a solution of pure Su^- . Data required for the calculation are summarized in Table 1. We calculated the following values: $\text{p}K_a(S_0) = 4.84$ for CiS and 4.64 for TrS, which are in good agreement with values reported in the literature [12], which are respectively 4.72 for CiS and 4.64 for TrS. In spite of the presence of two isobestic points, only a single $\text{p}K_a$ has been calculated in the pH range used in the study (pH 2–10).

3.2.2. Influence of pH on kinetics

The chemical stability of sulfonylureas in aqueous solution is markedly influenced by pH [3,6,7,9,10,13,14]. Consequently, in order to avoid the side effect of chemical hydrolysis, the photolyses were performed using a short illumination time (100 min for the longer irradiation). The influence of pH on the kinetic constants is represented in Fig. 4. One can note that for the two herbicides the photodegradation is faster for the lower pH, when the sulfonylureas are in their

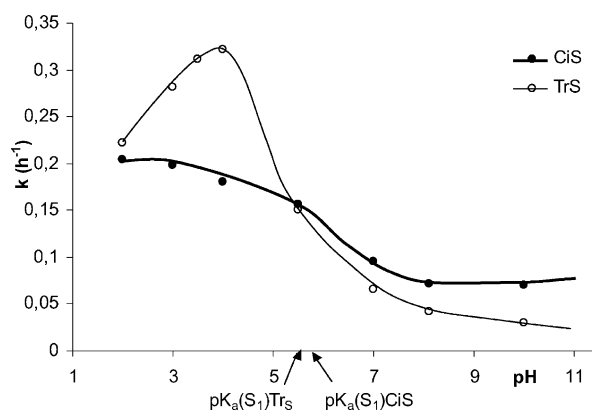


Fig. 4. Evolution of CiS and TrS kinetic constants as a function of the pH.

neutral form. The kinetic constant of CiS increases regularly with the decrease of the pH, ranging from 0.08 h^{-1} at pH 10 to 0.20 h^{-1} at pH 2, while the kinetic constant of TrS is at a maximum at pH 4 ($k = 0.32 \text{ h}^{-1}$) and then decreases at lower pH ($k = 0.22 \text{ h}^{-1}$ at pH 2). For both herbicides, the curves present an inflexion point for a pH value near 5.5.

The acid–base behavior of most organic molecules can be strongly affected by an electronic excitation. The $\text{p}K_a(S_1)$ values for the first singlet excited state can be estimated using the following relation derived from the Förster formula [11]:

$$\text{p}K_a(S_1) = \text{p}K_a(S_0) + \frac{0.625}{T} \Delta\bar{\nu} \quad (2)$$

where T is the absolute temperature and $\Delta\bar{\nu}$ the difference between the frequency of the maximum emission in the anionic and molecular forms (in cm^{-1}). In order to know the $\text{p}K_a(S_1)$ of CiS and TrS, the fluorescence spectra of both herbicides have been recorded at pH 2 and 10, with the excitation wavelength $\lambda_{\text{exc}} = 280 \text{ nm}$. The maximum emission wavelengths were $\lambda_{\text{em}}(\text{pH } 2) = 315 \text{ nm}$ and $\lambda_{\text{em}}(\text{pH } 10) = 311 \text{ nm}$ for both CiS and TrS. The $\text{p}K_a(S_1)$ values obtained from the formula (2) are 5.7 for CiS and 5.5 for TrS. It is deduced that the herbicides are slightly less acid in the singlet excited state. Moreover, one can note that the $\text{p}K_a(S_1)$ values correspond to the inflexion points of the kinetic constants curves (Fig. 4), suggesting that the first singlet excited state could have been involved in the photodegradation.

3.2.3. Influence of pH on the quantum efficiency

In our experimental conditions, several emission bands of the HPK lamp were involved, so we used the quantum efficiency notion (noted η) that took into account each emission wavelength of the lamp. Except in our preceding paper [7], to our knowledge, no photodegradation quantum yields of a sulfonylurea have been reported in water for wavelengths higher than 290 nm. The quantum efficiency values are presented Fig. 5 as a function of the pH. Broadly the values can be considered as high (between 0.03 and 0.12), compared with other classical pesticides such as anilide, s-triazine, organophosphorous or thiocarbamates that have

Table 1
Spectrometric data for the Förster cycle calculations

	CiS ($\lambda = 236 \text{ nm}$)	TrS ($\lambda = 221 \text{ nm}$)
A_{SuH} (pH 2)	0.0884	0.1423
A_{Su^-} (pH 8.1)	0.1710	0.1063
$A_{\text{SuH}+\text{Su}^-}$ (pH 5.5)	0.1560	0.1107

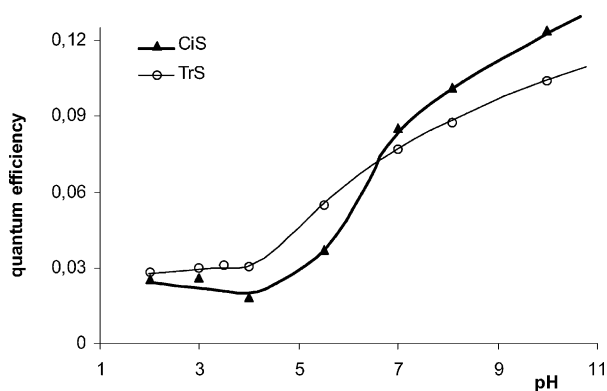


Fig. 5. Evolution of CiS and TrS quantum efficiencies as a function of the pH.

quantum efficiencies between 6×10^{-4} and 3×10^{-2} [15] for irradiation wavelengths >290 nm.

The quantum efficiencies of CiS and TrS are influenced by pH, as shown in Fig. 5. Indeed one notes that η increases when the pH of the solution increases. The anionic form is about 5 times more reactive than the molecular form (for example $\eta = 0.025$ at pH 2 for CiS and 0.124 at pH 10). These results might seem surprising since we have seen before that the kinetics were faster in acidic medium, so we could have expected that quantum efficiencies of sulfonyleureas were greater for acidic conditions. In fact the molar extinction coefficient of sulfonyleureas is higher in acidic medium (see Fig. 6, the ϵ values of CiS for the wavelength corresponding to the lamp emission). This could partly explain why the reaction rate is faster in acidic media. As for the evolution of the kinetic constant curves, the quantum efficiency curves exhibit an inflexion point for the pH corresponding to the $pK_a(S_1)$ of each herbicide (Fig. 5).

3.3. Influence of the wavelength

In order to evaluate the influence of the wavelength on the photochemical behavior of the sulfonyleureas, solutions of CiS and TrS have been irradiated into both the Pyrex and the quartz reactors with the pH adjusted to 7. In a similar manner, the quantum efficiencies have been calculated in

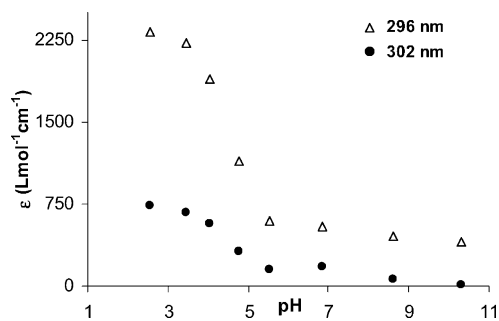


Fig. 6. Evolution of the molar coefficient extinction of CiS as a function of the pH at 296 and 302 nm.

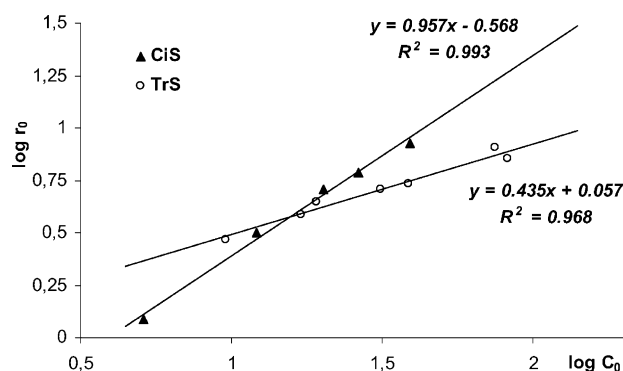


Fig. 7. Determination of the photodegradation kinetic order in the quartz reactor. Logarithm of the initial rate of CiS and TrS disappearance as a function of the logarithm of the initial concentration.

the quartz reactor, and in the two reactors the photoproducts have been identified and their evolution during irradiation established using HPLC.DAD.

3.3.1. Kinetics and quantum efficiency

In order to determine the kinetic order of the photolytic reaction, we have considered the following relation between the initial degradation rate r_0 and the initial herbicide concentration C_0 :

$$r_0 = \frac{-dC}{dt} = k C_0^\alpha \quad (3)$$

where α is the apparent order of the reaction, k is the apparent kinetic constant and C is the concentration of the herbicide at the instant t . The Fig. 7 shows the relationship between the logarithm of the initial concentration and the logarithm of the initial degradation rate in the quartz reactor. The plot indicates the kinetic order from the slope. In order to avoid any effect of the products formed during irradiation, calculations were done for herbicide conversion $<15\%$. The results reveal that kinetic orders are different for the two herbicides. Indeed, CiS presents a classical first order while for TrS, the kinetic order is 0.43. The result concerning TrS is unexpected in the case of a direct photodegradation and a fractional order is often a sign for a sequence of complex reactions. The same experiments previously conducted in the Pyrex reactor have indicated a first order for both CiS and TrS (slopes respectively 1.01 and 0.91 with correlation coefficients r^2 respectively 0.990 and 0.993).

The kinetic constants and the quantum efficiencies are collected Table 2. One can note that the transformations of CiS and TrS are faster and significantly more efficient for the lower wavelength, with a quantum efficiency 3.5 times more important in the quartz than in the Pyrex for CiS, and 2.2 times for TrS. This could indicate two different mechanisms of photodegradation in the two reactors.

3.3.2. Mechanisms of degradation

In order to compare the mechanisms of degradation in the two reactors, the photoproducts have been identified and

Table 2

Kinetic constants and quantum efficiencies of the photodegradation of CiS and TrS in the Pyrex and quartz photoreactors, in the phosphate buffer and in acetonitrile

Reactor	Solvent	CiS	TrS
Pyrex	Buffer (pH 7)	$k = 0.118 \pm 0.008 \text{ h}^{-1}$ $\eta = 0.04 \pm 0.02$	$k = 0.055 \pm 0.009 \text{ h}^{-1}$ $\eta = 0.05 \pm 0.03$
Pyrex	Acetonitrile	$k = 0.061 \pm 0.007 \text{ h}^{-1}$ $\eta = 0.009$	$k = 0.036 \pm 0.003 \text{ h}^{-1}$ $\eta = 0.03 \pm 0.01$
Quartz	Buffer (pH 7)	$k = 0.27 \pm 0.01 \text{ min}^{-1}$ $\eta = 0.14 \pm 0.02$	$k = 1.14 \pm 0.03 \text{ min}^{-1} \text{ mol}^{-1/\alpha} \text{ I}^{-1/\alpha}$ $\eta = 0.11 \pm 0.01$
Quartz	Acetonitrile	$k = 0.09 \text{ min}^{-1}$ $\eta = 0.065$	$k = 0.818 \text{ min}^{-1} \text{ mol}^{-1/\alpha} \text{ I}^{-1/\alpha}$ $\eta = 0.034$

their evolution during irradiation performed (details concerning their identification can be found in [7]). We present in this paper only the results obtained during irradiations of CiS but the same have been observed with TrS.

The results reveal that the same photoproducts were formed in both high and low wavelength experiments but their relative proportions were different. The chemical structure of the three main photoproducts (A), (B), and (C) formed during the degradation of CiS appear in the Scheme 1. The products (A), (B), and (C) are respectively a *s*-triazinosulfonic-urea acid, a *s*-triazinamide and a *s*-triazinamine. Figs. 8 and 9 present the evolution of (A), (B), and (C) formed respectively during the Pyrex and quartz irradiations.

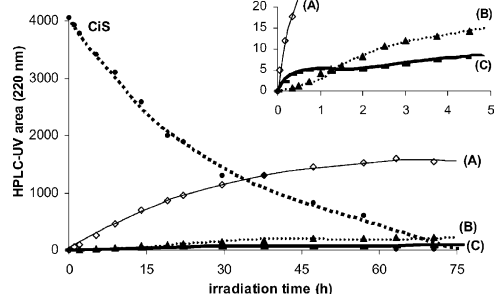
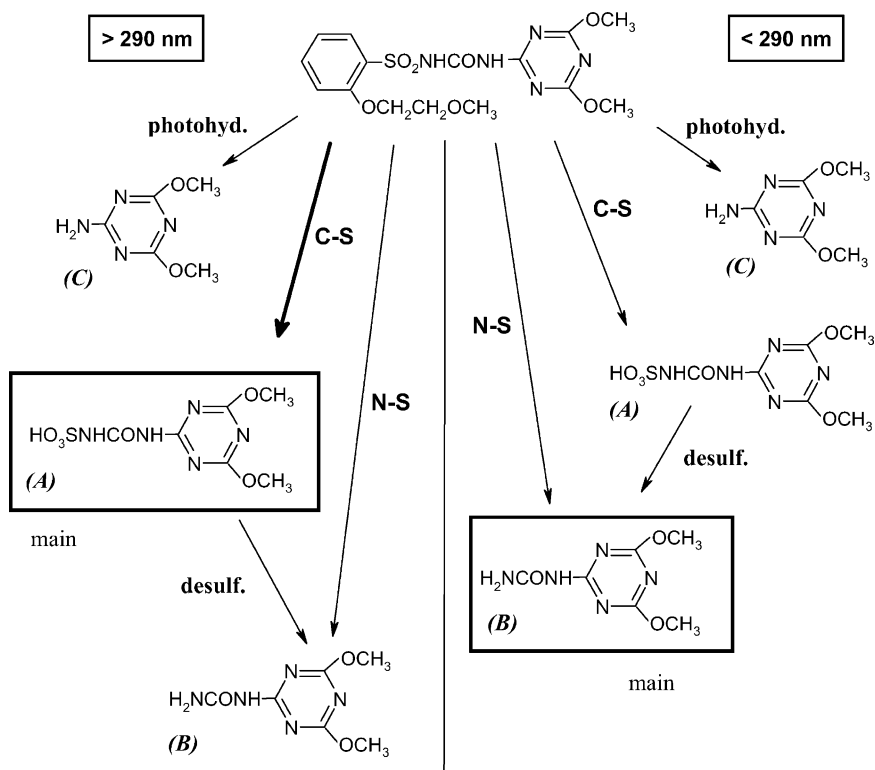


Fig. 8. Evolution of CiS, (A), (B), and (C) during the irradiation of CiS in the Pyrex reactor. Insert: zoom on the first hour of irradiation.



Scheme 1. Main pathways of photodegradation of CiS molecule in the Pyrex and the quartz reactors: photohydrolysis, carbon–sulfur cleavage, nitrogen–sulfur cleavage, photosulfonation.

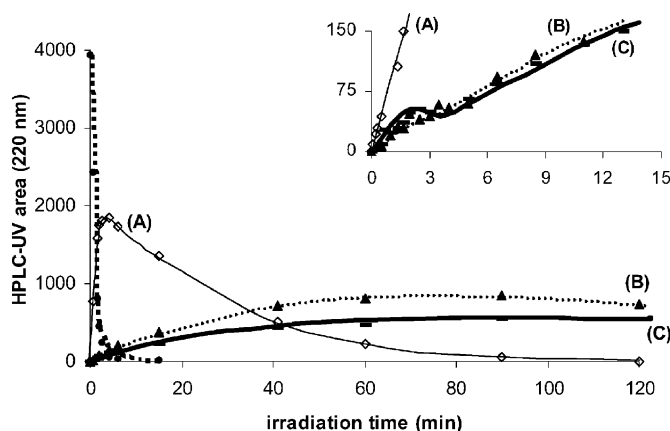


Fig. 9. Evolution of (A), (B), and (C) during the irradiation of CiS in the quartz reactor. Insert: zoom on the first minute of irradiation.

Some irradiations have been followed in acetonitrile. The kinetic results, presented in Table 2, show that acetonitrile has a significant effect on both the kinetics and the quantum efficiency. For example in Pyrex, the kinetic constants exhibit a 48% decrease for CiS and 34% for TrS in the presence of the solvent. In this reactor, the quantum efficiency of CiS is 4.5 times less important in acetonitrile than in the buffer and it is 1.7 times less important in the case of TrS. Concerning the photoproducts, we observed that only two products were formed: the *s*-triazinamide (B) and the second product was not identified. The photodegradation of sulfonylurea depends strongly on the experimental conditions.

The formations of (A), (B), and (C) correspond to several cleavages of the sulfonylurea molecule:

- The *s*-triazinosulfonic-urea acid (A) results from the carbon–sulfur cleavage, probably homolytic [16,17]. We can suppose that a charge transfer occurs between the two radicals produced, followed by water participation to form the final product (A). Without water, (A) is not present. The UV-visible absorption spectrum of (A) indicates that it absorbs only a small part of the irradiation >290 nm. Consequently in the Pyrex reactor it is photochemically stable and can accumulate in the solution, as shown in Fig. 9. On the contrary, at shorter irradiation wavelengths (A) is formed rapidly but it can also easily be transformed (Fig. 9). After only a few minutes of irradiation, its concentration rapidly decreases.
- The *s*-triazinamide (B) can be formed by two ways. The first one is the direct nitrogen–sulfur cleavage of the sulfonylurea herbicide, a classical homolytic reaction of amine photochemical deprotection [17]. The second way is a photodesulfonation of the photoproduct (A). Indeed Fig. 8 shows that (B) formation is very slow in the first hours of irradiation, then increases more rapidly probably because of (A) photodesulfonation. In acetonitrile, only the first way of formation occurs.

- The *s*-triazinamine (C) results from the photohydrolysis of the sulfonylurea link, a typical degradation pathway of sulfonylurea herbicides under irradiation [4–6,18–21].

We have evaluated the initial rate of formation of these three products, by considering the initial slope of the curves, during the first instant of irradiation (Figs. 8 and 9). The initial rates of formation of (A), (B), and (C) are noted A(Py), B(Py), and C(Py) in Pyrex and A(Qu), B(Qu), and C(Qu) in quartz. We have taken as reference, for each reactor, the initial rate of A formation. In these conditions, we obtained the following values:

In the Pyrex reactor:	In the quartz reactor:
A(Py) = 1.00	A(Qu) = 1.00
B(Py) = 0.04	B(Qu) = 0.24
C(Py) = 0.20	C(Qu) = 0.21

Regarding these values, it appears that the distribution of the products, and consequently of the corresponding cleavages of the molecules, is not the same in the two reactors. It is obvious that (A) is the main initial photoproduct whatever the reactor, but its production is in competition with formation of (B) in the quartz reactor. Indeed the formation of (A) is 25 times more rapid than the formation of (B) in Pyrex but only 4 times in quartz. So we can assume that the cleavage of the carbon–sulfur bond is favored in the Pyrex, and the nitrogen–sulfur cleavage favored in the quartz. On the other hand, the photohydrolysis leading to (C) seems not very sensitive to the choice of the reactor since $C(Py) \cong C(Qu) \cong 0.20$.

Caselli et al. [22] have reported that the sulfonylurea Chlorsulfuron could be considered as a bichromophoric molecule, with the benzenesulfonyl group representing one chromophore and the triazinic ring the second. In the case of chlorsulfuron, the authors reported that with wavelengths >280 nm the benzenesulfonyl chromophore is excited and 254 nm wavelength excites the *s*-triazinic group. The spectra of TrS in water (pH 2), 2-amino-4-methoxy-6-methyl-1,3,5-triazine and 2-chloroethoxybenzene (CEB) are presented in Fig. 10. These two latter compounds could be considered respectively as the *s*-triazinic and benzenic parts of the TrS molecule. The comparison between the three spectra shows that the band (I) of TrS overlaps the (AMMT) spectrum absorption with only a 5 nm shift, while the band (II) of TrS corresponds to the CEB part of the sulfonylurea, confirming that the (II) band is due to the benzenic ring.

In conclusion, the irradiations of sulfonylurea in the Pyrex reactor excite the benzenic chromophore of the molecule, favoring the carbon–sulfur cleavage of the link, and consequently the formation of the *s*-triazinosulfonic-urea acid (A) in the presence of water. Under these conditions the *s*-triazinamide (B) is mainly formed by desulfonation of (A). On the other hand the irradiations in the quartz excite both the benzenic and the *s*-triazinic parts of the sulfonylurea, inducing both the carbon–sulfur and the nitrogen–sulfur cleav-

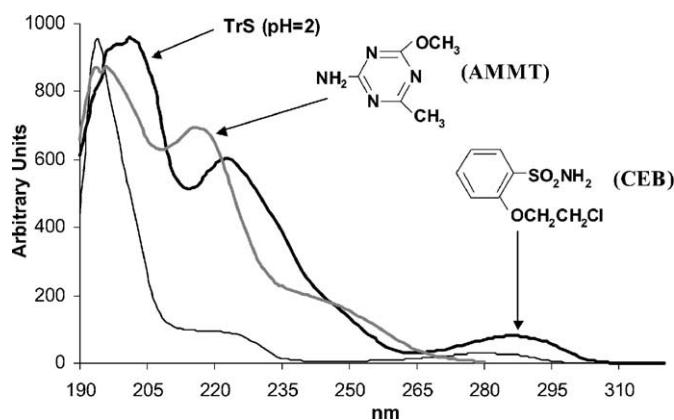


Fig. 10. Absorption spectra of TrS (pH 2), (AMMT), and (CEB), obtained with the HPLC.DAD chromatographic system (arbitrary units).

ages and increasing the formation of (B). These results obtained in water are summarized in a scheme of degradation of the sulfonylureas (Scheme 1). The results are different in acetonitrile suggesting that the observed photoproducts as well as the photodegradation pathway depend strongly on experimental conditions.

4. Conclusion

The sulfonylurea herbicides are easily photodegraded in both Pyrex and quartz reactors, with relatively high quantum efficiencies. The photochemical behavior of sulfonylureas depends on the pH. Indeed the photodegradations are faster in acidic medium, because of a higher molar extinction coefficient, but are more efficient in alkaline solutions, when the sulfonylurea molecules are in their anionic forms.

The sulfonylureas can be considered as bichromophoric molecules composed of benzenic and s-triazinic chromophores. The mechanism of photodegradation involves three main competitive pathways of which the predominant depends on the wavelength range conditions. The wavelengths >290 nm excite selectively the benzenic chromophore, leading mainly to the carbon–sulfur bond cleavage, whereas short wavelengths excite both benzenic and s-triazinic chromophores and make the nitrogen–sulfur cleavage more reactive. The third photodegradation pathway is the photohydrolysis of the sulfonylurea link, not very sensitive to the irradiation range choice.

As a consequence, the molecular structure of the sulfonylureas is an important parameter, particularly the nature of the benzenic substituent. Indeed electro-donor groups shift the absorption spectrum towards higher wavelengths, that permits a photodegradation for wavelengths superior than 290 nm, and also favor the carbon–sulfur cleavage.

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